

## PATENT SPECIFICATION



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## COMPLETE SPECIFICATION.

## Rust-Preventive Hydrocarbon Compositions.

I, JAMES GEORGE FIFE, M.Sc., Ph.D., F.I.C., Consulting Chemist and Chartered Patent Agent, of Bank Chambers, 329, High Holborn, London, W.C.1, a British Subject, do hereby declare the nature of this invention and in what manner the same is to be performed, (as communicated to me by Shell Development Company, a corporation organised under the Laws of the State of Delaware, United States of America, of 100, Bush Street, San Francisco, California, United States of America), to be particularly described and ascertained in and by the following statement :—

This invention relates to non-gaseous petroleum hydrocarbons such as gasoline, diesel fuel oils, lubricating oils, paraffin waxes, adhesive coatings, etc., containing small amounts of certain addition agents, which hydrocarbons possess very high anti-corrosion properties and greatly improved resistance to oxidation. The hydrocarbons of this invention are particularly well suited for use under conditions which normally result in rusting of at least part of the equipment in which the hydrocarbons are used.

It is known that the addition of relatively high-molecular weight polycarboxylic acids to lubricating oils imparts to the latter anti-corrosive properties. This has been described in the Specification No. 488,598, according to which polycarboxylic acids, such as polymerised oleic acid, alkylene succinic acids, etc., in lubricating oils are capable of protecting from corroding metals which are contacted by the oil.

Now my foreign Correspondents have discovered that the addition of small amounts of anti-oxidants to non-gaseous hydrocarbons containing high-molecular weight saturated aliphatic polycarboxylic acids enhances the anti-corrosive properties, provided the saturated aliphatic polycarboxylic acids are stable under the conditions to which the particular oil is exposed. It will of course be understood that the compositions of the present invention must be free from corrosion-inducing substances such as sulphonyl halides.

Any relatively high-molecular weight

saturated polycarboxylic acid, i.e., being free from olefinic double bonds, having 16 or more carbon atoms in the molecule and being sufficiently stable under ordinary lubricating conditions can be used, such as polymerised and hydrogenated fatty acids, e.g., voltolized and hydrogenated lauric, palmitic, stearic acids; oleic, ricinoleic, etc., acids polymerised with a halide polymerisation catalyst such as  $\text{BF}_3$  and subsequently hydrogenated; various alkylated aliphatic polycarboxylic acids such as succinic, glutaric, adipic, pimelic, suberic, azelaic, tricarballic, etc., acids. If desired, these acids may contain various substitution radicals such as hydroxyl, ether, amino, nitro, hydro-sulphide, sulphide, and halide radicals, the most important limiting factor being the necessary stability. In general, we prefer to use a saturated aliphatic dicarboxylic acid having the carboxyl radicals as close to each other as possible and as is consistent with the requirement for stability. Malonic acid and its alkyl derivatives are known to be unstable and, therefore, cannot be used.

Substituting monocarboxylic acids, such as stearic, oleic, arachic, behenic, etc., acids, for the above polycarboxylic acids results in oils having lesser stability and poorer rust protection properties. For example, such oils allow considerable rusting of the test strip in the Turbine Oil Rusting Test described later.

The dicarboxylic acids must not contain olefinic double bonds, as it has been found that their presence renders the acids susceptible to oxidation and resultant destruction with consequent loss of corrosion protective properties. Under some circumstances, this loss may be very rapid, and the presence of oxidation inhibitors does not prevent or materially retard this.

The most useful dicarboxylic acids for our purpose are alkylated succinic acids having 16 or more carbon atoms in the molecule and preferably those having more than 20 carbon atoms in the molecule. These may be produced by reacting olefines boiling above about  $300^\circ \text{C}$ .—such as may be obtained by cracking of paraffin wax or by dehydration of long chain fatty

- alcohols, etc.,—with maleic acid anhydride to produce an alkylene succinic anhydride, hydrogenating to produce the alkyl succinic acid anhydride, and hydrolyzing this anhydride to produce the corresponding acid. Such acids have been described in Specification No. 488,597. As is known, polycarboxylic acids of less than 16 carbon atoms in the molecule have little or no corrosion inhibitor properties.
- The anti-oxidants which we have found to be effective in combination with the saturated dicarboxylic acids may be hydroxy or amino aromatic compounds.
- Suitable oxidation inhibitors are, for example, mixed alkyl phenols, the xylenols, the 2,4,6-trimethyl phenol, the pentamethyl phenol, various methyl ethyl phenols or phenols containing isopropyl, isobutyl, isoamyl, tertiary butyl, tertiary amyl, etc., radicals; alpha naphthol, alkylated naphthols, various phenols containing amino radicals such as paramino phenol, ortho-amino phenol, parabenzy amino phenol, alkyl amino phenols; aromatic amines, as diphenylamine, alpha or beta naphthylamine, phenyl alpha naphthylamine, alpha beta dinaphthylamine, etc. Preferred inhibitors are, on the one hand, the alkyl phenols having not less than two alkyl radicals located in the 2,4-and/or 6-positions of the phenol, at least one of the alkyl radicals being a tertiary alkyl radical and, on the other hand, the secondary amines having two aromatic nuclei attached to the nitrogen.
- The amounts of both the anti-corrosive and anti-oxidant agents may vary considerably, depending upon the use to which the oil is put. Normally, the amounts are much smaller than had heretofore been considered necessary for good corrosion protective properties and good oxidation stability. This is so because the two inhibitors augment each other, both with regard to corrosion and oxidation inhibition. Thus the presence of the corrosion inhibitor which has no known anti-oxidant property results in an increased effectiveness of the anti-oxidant; and likewise, the presence of the oxidation inhibitor which has no substantial anti-corrosive properties vastly improves the corrosion protecting powers of the particular corrosion inhibitors.
- Heretofore it was believed that the quantities of corrosion inhibitors required to give good corrosion protection were of the order of about .25% to 5%. While we may employ quantities of this magnitude, we have found that in combination with the anti-oxidant considerably smaller amounts of the polycarboxylic acid ranging from between .001% to .1% are usually sufficient. The lasting effectiveness of these small amounts of polycarboxylic acids is dependent upon the presence of the anti-oxidant. The amount of the anti-oxidant, while useful up to about 5%, rarely needs to exceed 1%, and effective amounts, when used in combination with the corrosion inhibitor, usually vary from .001% to 1%.
- It is usually desirable to obtain good corrosion and oxidation protection with the smallest effective quantities of the inhibitors. Polycarboxylic acids suitable as corrosion inhibitors as well as oxidation inhibitors have the undesirable effect of lowering the interfacial or surface tension of the hydrocarbon oils to result in potential emulsion difficulties when the oil comes in contact with moisture or water in crank-cases, tanks, jets, etc., and it is desirable to minimize this effect as much as possible by reducing the quantities of the inhibitors to within the limits indicated. In this connection, it is interesting to note that the reduction of the surface tension caused by the addition of both the polycarboxylic acids and the anti-oxidants is considerably less than would be expected from the known effects on interfacial tension of the individual inhibitors.
- It is of advantage to have the anti-corrosion and anti-oxidant properties reside in two different types of compounds, because the anti-oxidant becomes oxidized in the course of its useful life. If the anti-oxidant were at the same time the anti-corrosion agent, then all protective action would be destroyed at once, since oxidation of the corrosion inhibitor renders it ineffective, as pointed out above. Moreover, since the anti-corrosion agents operate by way of coating the metal surface, the oil as a result becomes depleted of the corrosion inhibitor and also of the oxidation inhibitor if both inhibiting properties are combined in one compound. The absence of the anti-oxidant would then permit more or less rapid oxidation of the oil and formation of relatively strong acids which would have a tendency to destroy the protective coating.
- Some of our inhibiting lubricating oils are particularly useful, for example, as turbine oils.
- In the lubricating of turbines, oil is constantly circulated from a storage system connected with the turbine to the various parts to be lubricated and back to the storage. The oil is used over a long period of time, during which time it comes in contact with the atmosphere as well as with water. This contact has a detrimental effect on the qualities of the oil in that the oil oxidizes, thereby forming acid compounds which reduce the interfacial tension

between water and the oil greatly. An oil so oxidized tends to emulsify with the water. Moreover, the presence of water frequently causes rusting, particularly to portions of the governor mechanism. Metallic iron and copper, which are always used in the construction of turbine oiling systems, have a catalytic effect on oil oxidation. A good turbine oil must, therefore, be substantially rust-preventive in the presence of water, must be highly resistant to oxidation in the presence of iron and copper, and must possess a reasonably high interfacial tension against water.

Excellent turbine oils can be produced from well refined lubricating oils of the proper viscosity range, which may be about 75—750 Say. Univ. seconds at 100°F., by adding to them about .001% to .1% of a polycarboxylic acid of the type hereinafter described, and, in addition .001% to 1.0% of an oxidation inhibitor for hydrocarbon oils.

The combined effects on oxidation stability of small amounts of a dicarboxylic acid of the above type and a typical inhibitor is well illustrated by the curves shown in the accompanying drawing, in which neutralization number of an oil having a Say. Univ. viscosity of 150 at 100°F is plotted against time of exposure to oxygen under a standard set of conditions. Curve 1 shows the oil without addition agent. Curve 2 shows the oil containing .01% of 2,6-ditertiary butyl-4-methyl phenol, and curve 3 shows the same oil containing .01% of the same alkyl phenol, and, in addition, .01% of an alkyl succinic acid produced by condensing maleic acid anhydride with an  $\alpha$ -C<sub>18</sub> olefine and hydrolysing and then hydrogenating the condensation product. As will be noted, the addition of the succinic acid greatly enhances the anti-oxidant effect of the inhibitors. Further, the oil containing both the succinic acid and the inhibitor was altogether rust-preventive in a Turbine Oil Rusting Test, which is carried out as follows: a strip of clean bright steel is suspended in a sample of oil contained in a glass beaker equipped with a glass stirrer. The oil is heated to 75°C., agitated for 30 minutes, and 10% by volume of distilled water is added. The oil is stirred for 48 hours while maintaining the temperature and water concentration, and the amount of corrosion of the test strip is noted.

The oils of this invention may be further improved by incorporating therein in addition from about 1% to 10%, and preferably about 3% to 6%, of so-called blowdown oil from coke produced in the cracking of hydrocarbon oils when running

to coke.

Blowdown oil is a highly aromatic oil obtained by steam-blowing coke produced in the cracking of hydrocarbon oils when running the residue to coke in the reaction chamber. Whenever a chamber is filled with coke, it is taken out of circulation and steam is blown through it while it is hot. A highly aromatic oil having a boiling range of gas oil and higher is driven off. The first fractions of this oil comprise predominantly alkyl naphthalenes and the later fractions contain large amounts of more highly condensed aromatics, i.e. alkylated anthracenes, phenanthrenes, picones, chrysenes, etc., as well as tarry matter. Upon redistillation a clear yellow oil is produced, which is the blowdown oil. If relatively high boiling fractions are included, white to yellow crystals may separate on standing. As a rule, the aromatic content of the blowdown oils is considerably above 50%, specific dispersions ranging from about 200 up to 500.

It is understood that the compounded lubricating oils hereinbefore described can be used in the lubrication of machinery other than turbines as well. Thus they may be used in internal combustion engines or in the lubrication of a great variety of sensitive equipment. The rust corrosion protective properties of the oil render it especially valuable wherever danger of corrosion or rusting exists, as in the lubrication of open bearings which may be exposed to moisture or atmospheric conditions. All that may be necessary is to adjust the viscosity of the oil to the individual needs. The latter is well within the skill of the average lubrication engineer.

Diesel fuels such as those having Say. Univ. viscosities of 32 or 350 seconds at 100°F. when inhibited with some of the compounds described above possess not only excellent non-corrosion characteristics but also a greatly reduced tendency to clog orifices of injection pumps, fuel filters, etc. This latter improvement is much greater than is due to the presence of the oxidation inhibitor and is probably due to a reduction of a metal-catalytic effect, because of the polycarboxylic acids deposited on the metal surfaces of containers in which diesel fuel is stored.

Diesel fuels, like turbine oils, must be substantially rust-preventive, because diesel engines, especially those having unit type injectors, often encounter trouble in the fuel injectors due to corrosion of closely fitted injector parts.

The corrosion effect of our inhibited diesel fuels upon the metal plungers of diesel engines was determined by immersing the clean, polished metal for 200 hours in baths maintained at 200°F. The baths

contained inhibited diesel fuel and water and were agitated by blowing air through

them.

Results were as follows:

5

## Corrosion:

Alkyl phenol inhibited fuel + 1% water + air Some corrosion

Alkyl phenol inhibited fuel + 1% water + air  
+ .001% of a C<sub>22</sub> alkyl succinic acid Slight corrosion

10

Alkyl phenol inhibited fuel + 1% water + air  
+ .01% of a C<sub>22</sub> alkyl succinic acid No corrosion.

Gasolines are always subject to oxidation due to contact with air in the presence of metallic iron, copper, etc., which are oxidation catalysts. During storage in tanks, drums, etc., such fuels often come in contact with water which not only increases the rate of deterioration of the gasoline, but also causes rapid rusting and decay of the storage vessels. This problem is of particular importance in the shipment and storage of aviation gasolines in drum lots in tropical countries. The presence of a trace of our polycarboxylic acids together with an oxidation inhibitor completely overcomes this difficulty. The use of the smallest effective amounts of the polycarboxylic acids in aviation gasolines in particular is quite important in that larger quantities tend to deposit in manifolds and in valves and valve seats of gasoline engines in which the fuels are used. The rust-preventive combination of a saturated aliphatic polycarboxylic acid and an oxidation inhibitor is also useful in protective or adhesive coatings used to protect metals during storage, shipment, etc., to stabilize the coating itself against deterioration due to oxidation and to give added protection to the base material against the combined effects of air and water. The rust-preventive combination is particularly effective where the thin coating is not completely impervious to air and water.

Examples of such coatings are adhesives, such as solutions of mixtures of polymerization products of butadiene or isoprene and balata of gutta-percha used for bonding rubber to metal; various resins, for example, phenol-formaldehyde resins used to varnish metal parts or to cement thin metal sheets, translucent or petroleum plastics, such as petroleum resins, albino asphalts, etc., used as metal protective coatings; wax polishes containing paraffin waxes, etc.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, (as communicated to me

from abroad) I declare that what I claim is:

1. Rust-preventive compositions free from corrosion-inducing substances comprising predominantly non-gaseous hydrocarbons containing dissolved small amounts each of a stable saturated aliphatic polycarboxylic acid having at least 16 carbon atoms in the molecule and an oxidation inhibitor for said hydrocarbons.

2. A composition as claimed in claim 1, wherein the non-gaseous hydrocarbons are a hydrocarbon oil.

3. A composition as claimed in claim 1, wherein the non-gaseous hydrocarbons are a lubricating oil.

4. A composition as claimed in claim 1, wherein the non-gaseous hydrocarbons are a turbine oil.

5. A composition as claimed in claim 1, wherein the non-gaseous hydrocarbons are a Diesel fuel oil.

6. A composition as claimed in claim 1, wherein the non-gaseous hydrocarbons are a hydrocarbon motor fuel.

7. A composition as claimed in claim 1, wherein the non-gaseous hydrocarbons are an albino asphalt.

8. A composition as claimed in any one of the preceding claims, wherein the amount of said aliphatic polycarboxylic acid is .001% to .1% and the amount of said oxidation inhibitor is .001% to 1%.

9. A composition as claimed in any one of the preceding claims, wherein the oxidation inhibitor is selected from the group consisting of hydroxy and amino aromatic anti-oxidants.

10. A composition as claimed in any of the preceding claims 1 to 8, wherein the oxidation inhibitor is a phenolic oxidation inhibitor.

11. A composition as claimed in any one of the preceding claims 1 to 8, wherein the oxidation inhibitor is an alkyl phenol having not less than 2 alkyl radicals, at least one of which is a tertiary alkyl radical.

12. A composition as claimed in any one

of the preceding claims 1 to 8, wherein the oxidation inhibitor is a di-aryl amine.

13. A composition as claimed in any one of the preceding claims, wherein the

5 aliphatic polycarboxylic acid is a saturated alkyl succinic acid having at least 16 carbon atoms in the molecule.

14. A composition as claimed in any one of the preceding claims 1 to 12, wherein  
10 the polycarboxylic acid is a hydrogenated and hydrolyzed product of the reaction of an olefine with maleic acid anhydride said product having at least 20 carbon atoms in the molecule.

15 15. A composition as claimed in any one of the preceding claims 1 to 12, wherein the polycarboxylic acid has its carboxyl radicals separated by a link consisting of 2 carbon atoms.

20 16. A composition as claimed in any one of the preceding claims 1 to 12, wherein

the polycarboxylic acid is an alkyl phthalic acid having at least 16 carbon atoms in the molecule.

17. A composition as claimed in any  
25 one of the preceding claims 1 to 4, which contains in addition 1% to 10% of a blow-down oil and wherein the aliphatic carboxylic acid is a dicarboxylic acid.

18. A composition as claimed in claim  
30 4, wherein the turbine oil is a refined mineral lubricating oil having a viscosity at 100°F. of 75 to 750 Saybolt Universal seconds.

Dated this 29th day of May, 1942.

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and

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Agents for the Applicant.

2<sup>nd</sup> Edition

[This Drawing is a reproduction of the Original on a reduced scale.]

Neutralization  
Number

